

UDC 666.762.63

## SYNERGISTIC APPROACH TO SINTERING BINARY OXIDE MIXTURES FOR PRODUCTION OF $\text{SrZrO}_3$ -BASED CERAMICS

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Translated from *Steklo i Keramika*, No. 12, pp. 12–15, December, 2004.

The possibility of producing ceramics based on strontium zirconate combining synthesis and sintering in a single stage is discussed in the context of a synergistic approach. Conditions enabling one to produce ceramics with a certain structure are proposed.

Ceramics based on strontium zirconate has a number of valuable properties: high melting point, high resistance to alkali melts, electroinsulating properties under elevated temperatures, etc. [1]. However, its use in industry is limited due to its two-stage production process: first,  $\text{SrZrO}_3$  is synthesized and ground, and then articles are molded from it and fired.

Research was carried out for the purpose of combining the synthesis and sintering of strontium zirconate in a single stage [2]. However, this involves certain difficulties. In solid-phase sintering of  $\text{SrZrO}_3$  the preform volume increases significantly and leads to diffusion porosity. This is a consequence of the significant difference between the diffusion coefficients of  $\text{Sr}^{2+}$  and  $\text{Zr}^{4+}$  cations, which results in Kirkendall and Frenkel effects and the formation of diffusion porosity. Since sintering of ceramics in the single-stage process starts before the end of the chemical reaction, a rigid skeleton is formed from non-reacting grains of the initial oxides ( $\text{SrO}$  and  $\text{ZrO}_2$ ) and the reaction product. In the course of further sintering, the surface tension forces are not sufficient for destroying this skeleton and the porosity remains substantial even after protracted firing [3].

Besides the known Kirkendall and Frenkel' effects, the difference in the diffusion rates of the oxide cations that react and form a complex oxide leads to the formation of a solid solution of the oxide containing the cation with the lower diffusion rate in the complex oxide being synthesized ( $\gamma$ -nonstoichiometry) and a phase rich in the oxide (or consisting of the oxide) with the faster-diffusing cation [4]. The formation of  $\gamma$ -nonstoichiometry and the phase with an excess of the oxide with the faster-diffusing cation is a consequence of the self-organization of the reacting oxide system. The process intensifies with increasing degree of nonequilibrium, as the

particle size of the reacting oxides decreases. This phenomenon can be used to identify the faster-diffusing cation in the synthesis of complex oxides from highly disperse powders of simple oxides, which needs to be known for the choice of dopants [5]. For instance, when sintering is combined with the chemical reaction, to obtain dense ceramics the mass flow of the reacting oxide cations has to be balanced, i.e., fast cations have to be slowed down and/or slow cations accelerated.

When complex oxides are sintered simultaneously with the chemical reaction of their formation, in addition to the three main bifurcations [6], another one is added which is related to the volumetric modification caused by the chemical reaction. The chemical reaction influences the evolution of the skeleton structure and raises the degree of nonequilibrium of diffusion mass transfer. This bifurcation in fact acts as the first main bifurcation of sintering without the chemical reaction, when local compactions formed in molding and drying disappear and new ones arise (an abrupt modification of the skeleton structure). As a consequence of self-organization, a skeleton is formed consisting of compacted areas and large pores between them, which cannot be removed at the final stage of sintering; therefore, high-density ceramic is impossible to produce. This may be interpreted as the accumulation of a part of the excess energy by the system, which is spent on the formation of new surfaces (pores).

The multistability of the system with significantly different stable states is the reason for the poor reproducibility of ceramic structures [7]. Such low reproducibility can be eliminated by controlling signals that have an effect on the system [8, 6].

To eliminate multistability in the course of the chemical reaction, a mixture of two presynthesized compositions was used: a low-temperature composition (LTC) and a high-temperature composition (HTC). This technique was applied to obtain a heat-resistant refractory made of strontium zircon-

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ate. The overall composition of the mixture corresponded to the desired chemical compound. The LTC selected for the SrZrO<sub>3</sub>-based refractory was a granular filler of the following composition (here and elsewhere, wt.%): 45.16 SrO and 54.84 ZrO<sub>2</sub>; the HTC was a combined binder of the composition (wt.%): 40 Sr<sub>4</sub>Zr<sub>3</sub>O<sub>10</sub>, 10 mixture of 45.16 SrO and 54.84 ZrO<sub>2</sub> (weight ratio of grain filler to combined binder 1 : 1), and this choice provided for a refractory with a fragmentary structure, whose heat resistance based on 850°C – water thermal cycles grew from 2 (without the chemical reaction) to 23 cycles [9].

The purpose of our study was to analyze the effect of various controlling influences on the formation of the structure of ceramics from strontium zirconate under sintering combined with the chemical reaction and to estimate their efficiency with respect to achieving stable properties.

The experiment used SrCO<sub>3</sub> of the “analytically pure” grade and ZrO<sub>2</sub> of grade TsRO-1.

The preparation of materials and batch preparation were performed using different schemes:

1) powders ZrO<sub>2</sub> and SrCO<sub>3</sub> taken in a stoichiometric ratio were milled in a polyethylene drum with zirconium dioxide balls using moist grinding (materials : balls : water ratio = 1 : 2 : 1);

2) zirconium dioxide powder was first subjected to moist milling in a planetary mill (3 min) and then followed scheme (1);

3) a mixture prepared according to schemes (1) or (2) was milled in a planetary mill (3 min, dry milling);

4) initial components jointly milled in a planetary mill (3 min, dry milling);

5) powders separately ground in a planetary mill and then subjected to joint milling also in a planetary mill;

6) a 20% additive (calculated on the batch) of previously synthesized SrZrO<sub>3</sub> that had been produced by firing a stoichiometric mixture for 2 h at 1300°C was mixed in a ball mill with a mixture produced by scheme (1) or scheme (2);

7) the same was carried out in a planetary mill;

8) briquettes were compressed from strontium carbonate at a pressure of 300 MPa (PVA solution used as a binder); then these briquettes were milled and screened, producing granules of different fractions, which were mixed with ZrO<sub>2</sub> power in the polyethylene drum using rubber milling bodies to intensify mixing and diminish the milling of the granules.

Each mixture, except the one prepared according to scheme (8), was used to prepare molding powder adding PVA solution as a binder (1% converted to dry material) and sifting it through a No. 05 sieve. The molding powder was used to mold samples shaped as tablets or bars at a molding pressure of 100 MPa. The molded samples were fired in different conditions varying the firing regime and medium. To create a reducing medium, the samples were placed in a crucible, into which burning-out additives were placed as well, and then fired with the lid closed. At the same time, other samples were fired in a boat-shaped open crucible with the firing medium being oxidizing. As for the firing regime, spe-

TABLE 1

Batch preparation method	Open porosity, %, of SrZrO <sub>3</sub> ceramics			
	in reducing medium at heating rate, K/min		in oxidizing medium at heating rate, K/min	
	5	1	5	1
Scheme (8), granules of size, mm:				
0.125 – 0.500	65.0	62.0	64.0	63.0
below 0.125	64.0	64.0	62.0	56.0
Scheme (1)	42.0	31.0	27.0	26.0
Scheme (6)	24.0	10.0	6.0	3.4
Scheme (3) (after scheme (1))	29.0	18.0	2.8	2.1
Scheme (5)	–	13.0	–	1.5

cial attention was focused on the heating rate in the temperature interval of 900 – 1350°C (the interval of SrZrO<sub>3</sub> formation), therefore, we differentiated the “fast” (heating rate 5 K/min) and the “slow” (heating rate 1 K/min) regimes.

After the end of firing, water absorption and porosity of the samples were determined using the hydrostatic weighing method. The measurement results are given in Table 1.

It can be seen that the porosity of samples is highly sensitive to the batch preparation method and the firing conditions.

When the initial components were milled in a ball mill (scheme (1)), it was impossible to produce dense samples. However, the dependence of the porosity of ceramics on the firing conditions was established: samples in the reducing medium were always more porous than in the oxidizing medium, and a decreased heating rate within the temperature interval of 900 – 1350°C led to decreased porosity. It should be noted that the effect of the heating rate is especially perceptible in the reducing medium. Most probably the main reason for this phenomenon is the effect of the partial pressure of CO<sub>2</sub> on the reaction of decomposition of SrCO<sub>3</sub>. The presence of CO<sub>2</sub> in the gaseous phase ought to shift the chemical reaction of the decomposition of SrCO<sub>3</sub> to the higher-temperature range and its absence to the lower-temperature range.

As a consequence of moist milling and decomposition of polyvinyl alcohol, OH groups penetrate into SrCO<sub>3</sub>. They may penetrate into SrO emerging in the decomposition of SrCO<sub>3</sub>. This is facilitated by the oxidizing medium. The presence of OH groups and, accordingly, cation vacancies activates the diffusion mass transfer in SrO:



Such SrO reacts with ZrO actively and at a lower temperature. The chemical reaction is shifted to the lower-temperature range, and the system, even before the beginning of sintering, has time to partially dissipate the chemical reaction energy and partly accumulate this energy in the form of pores

and structural defects of the  $\text{SrZrO}_3$  structure. The lower temperature of  $\text{SrZrO}_3$  formation is responsible for the fact that the diffusion processes of skeleton sintering are slowed down as well. The crystals forming the skeleton have no time to perfect their structure and preserve a substantial quantity of point defects for subsequent compaction. Such a skeleton is capable of further consolidation; therefore, dense ceramics can be obtained after firing.

The reducing medium retards the decomposition of the carbonate, whereas the emerging products ( $\text{CO}_2$ ) react with OH groups and replace them. In this case the decomposition of strontium carbonate and the synthesis of zirconate are shifted to the high-temperature range, but are more intense. The temperature interval of the chemical reaction is narrower; accordingly, the system has no time to dissipate the chemical reaction energy. The system is forced to accumulate energy, mainly not in the form of defects of the  $\text{SrZrO}_3$  structure, but in forming pores. The structure defects in these conditions intensely migrate to the boundaries of the nearest pores. At the same time, the areas forming the skeleton become condensed and their structure is perfected to a significantly greater extent than when fired in a reducing medium. This skeleton later has poor sinterability; therefore, dense ceramics cannot be obtained.

Thus, it is necessary for SrO formed after the decomposition of  $\text{SrCO}_3$  to have a sufficient time to enter the chemical reaction of  $\text{SrZrO}_3$  production before the beginning of the diffusion processes in sintering, which perfect the areas integrating the skeleton. This can be facilitated by a decrease in  $\text{CO}_2$  partial pressure (the oxidizing medium in firing) and a decrease in the heating rate; therefore, the ceramics fired in the oxidizing medium at the heating rate of 5 K/min is always less porous than in a reducing medium with a temperature rise of 1 K/min (Table 1). Even a slight increase in  $\text{CO}_2$  pressure caused by firing of samples in a crucible under a closed lid is sufficient for a perceptible increase in ceramics porosity.

When mixtures prepared in accordance with scheme (1) or scheme (2) were additionally milled in a planetary mill (scheme (3)), the samples after firing became much denser (Table 1). The results here depend significantly on the firing conditions: in a reducing medium the open porosity reached 18–29% (depending on the heating rate) and in an oxidizing medium it was only 2–3%. However, after protracted storage of the batch (a few months) the samples became less dense.

It is logical to assume that sintering would improve with decreasing grain size. However, when strontium carbonate and zirconium dioxide preliminarily milled in a planetary mill were mixed in a ball mill (scheme (2)), the results were visually identical to the ones obtained without preliminary milling. Most probably, dry milling of mixtures in a planetary mill generates mechanical activation [10]. This agrees with the deterioration of the results after the long-term storage of prepared powder.

Dense samples were produced as well by mixing components in a planetary mill (schemes (4) and (5)) and by firing in a sufficient amount of oxygen.

The addition of presynthesized  $\text{SrZrO}_3$  to a stoichiometric mixture of  $\text{SrCO}_3$  and  $\text{ZrO}_2$  (scheme (6)) as well provides for the production of a dense material. It was assumed that the introduction of  $\text{SrZrO}_3$  powder particles into the mixture would make it possible to split the preform volume into cells, in which the stoichiometric mixture of  $\text{SrCO}_3$  and  $\text{ZrO}_2$  would be located. The cell size was expected to be small and the volumetric changes inside each cell would be smaller as well. This should provide for denser ceramics.

Samples with an additive of presynthesized  $\text{SrZrO}_3$  has higher density than samples produced according to scheme (1) fired under similar conditions. However, compared to samples prepared with milling in a planetary mill (schemes (3)–(5)), the density of samples after firing in a reducing medium was slightly higher, but the spread in values was greater as well. Thus, this effect was insufficient compared to the effect of the partial pressure of  $\text{CO}_2$  in firing. However, the shrinkage was lower (24% in scheme (3) and 19% in scheme (6)) and, consequently, the probability of the formation of cracks and deformations of products in firing was lower as well. When this batch was ground in a planetary mill or when the components were mixed directly in the planetary mill (scheme (7)), the results were more stable. The porosity of the samples was virtually identical to the porosity of samples obtained in schemes (3) and (4), whereas the firing shrinkage was slightly lower.

An attempt was made to decrease the activity of SrO before its reaction with  $\text{ZrO}_2$ . For this purpose zirconium dioxide was subjected to moist milling to obtain a maximum degree of dispersion. Strontium carbonate was used to compress preforms which were crushed to obtain granules. The mixing of these granules with zirconium dioxide was performed by dry milling in a ball mill using rubber corks instead of balls, to preserve strontium carbonate granules. It was expected that SrO released under heat treatment would sinter in the form of large crystals before its reaction with  $\text{ZrO}_2$  and would lose its activity. However, the chemical reactions started earlier than SrO sintering.

Samples produced from granulated strontium carbonate had high porosity (63–65%) regardless of the firing regime and medium. The porous material produced in this way can presumably be used in industry, for instance, as high-temperature heat insulation. It is not necessary to use burning-out additives in its production. The shrinkage of such samples in firing is either zero, or the sample size increases slightly (4–7%). It was found in the study that the maximum possible size of  $\text{SrCO}_3$  granules is 0.5 mm. Samples in which strontium carbonate was introduced via granules of size 0.5–1.0 mm crumbled in firing. By controlling the size of strontium carbonate granules it is possible to modify the structure of ceramics (amount of pores and their size distribution).

Thus, the most significant impact on the evolution of the structure in the production of porous ceramics under the conditions considered was the granulation of SrCO<sub>3</sub>, whereas the effect of the firing medium, was insignificant. In producing dense ceramics the most perceptible was the impact of the firing medium and the mixture of components had to be activated in the planetary mill. The weakest of all factors considered was introducing presynthesized powder into the mixture. The dry milling of the initial components in a planetary mill made it possible to produce dense SrZrO<sub>3</sub>-based ceramics combining synthesis and sintering.

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